The University of Chicago

ELECTROMERS OF 2-PENTENE

A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1929

By
MELVIN ORVIL FOREMAN

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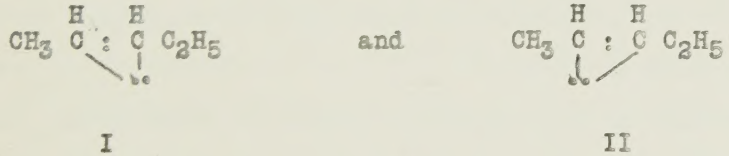
PURPOSE OF WORK

The application of the theory of partial polarity of the ethylene bond developed by Kharasch and Darkis[1] is in accord with the facts recorded in the literature with the exception of the addition of hydrogen bromide to 2-pentene.[2] The theory of partial polarity predicts the formation of 2-bromopentane as the chief product of the reaction. Lucas and Moyse obtained, however, a mixture of 2-bromopentane and 3-bromopentane in which the latter constituted 78% of the mixture. Since this reaction is the only exception in the literature to the facts supporting the theory of partial polarity, it was made an object of careful and extended study by Kharasch and his co-workers. As a result of this study, the existence of electromers of 2-pentene has been advocated. These electromers differ only in the position of the two electrons of the double bond which determine the manner in which they add unsymmetrical reagents, viz:



I and II

Form I, which we have reason to believe is the more stable, adds hydrogen bromide in accord with the predictions of the theory of partial polarity. The present paper describes a portion of the evidence in favor of the existence of such electromers and is confirmatory to the work previously carried out

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1. Kharasch and Darkis, Chem. Rev. V, 4:571 (1928)
2. Lucas and Moyse, J. Am. Chem. Soc. 47:1459 (1925)

in isolating and proving the structure of these compounds.

Theories Relating to Addition Reactions at Double Bonds.

A. Empirical Rules.

Before the advent of the electronic conception of valence, empirical rules were developed which predicted the addition of an unsymmetrical reagent, i. e., hydrogen halides, etc., to an ethylene bond. Markownikow's[3] rule states that in the addition of a hydro-halide to an ethylene bond, the halogen becomes attached to that carbon atom which is poorest in hydrogen. This rule was later extended by Saytzeff[4] to those ethylene derivatives in which each carbon atom of the double bond is joined to the same number of hydrogen atoms. In such cases, according to Saytzeff, the halogen becomes attached to the carbon nearest the end of the hydrocarbon chain. Markownikow's rule is not applicable to 2-pentene, $CH_3C{::}^{H}_{H}CC_2H_5$, for each carbon of the double bond is attached to one hydrogen atom. Saytzeff's rule predicts the formation of 2-bromopentane when hydrogen bromide is added.

Because of the empirical nature of these rules, they are necessarily restricted to the class of compounds, the aliphatic hydrocarbons, which gave rise to them. When correctly applied they predict accurately addition of unsymmetrical reagents to the double bond of ethylene derivatives. Other classes of compounds containing a double bond offer numerous exceptions, however, to these rules.

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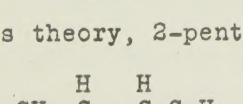
3. Markownikow, Ann. 153:256 (1870)
4. Saytzeff, Ann. 179:297 (1875)

The electron theories of the double bond make possible a broader understanding of these addition reactions. The application of theories of ethylene bond additions, based on this newer conception of the character of valence forces, should be capable of universal application. Several such theories have been advanced to explain the addition reaction of unsymmetrical reagents to double bonds. We shall consider only two of these theories, the theory of partial polarity of the double bond,[1] and the Lucas extension[5] of the Lewis hypothesis.[6] Reference should be made to the work of Carothers[7] in this field of theoretical organic chemistry. However, the latter's views do not lend themselves to ready application and will not be discussed here.

B. The Lucas Extension of the Lewis Hypothesis.

The theoretical speculations of Lucas follow closely the Lewis hypothesis. They differ basically, however, from the theory of partial polarity. We shall attempt to emphasize in this paper the fundamental differences existing between the two theories. According to Lucas, a strongly electronegative atom or radical tends to draw toward it, not only the electrons constituting the bond joining it to the molecule, but also the valence electrons constituting chemical bonds in the vicinity of it. According to this theory, 2-pentene possesses the following structure:



This structure re-

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5. Lucas and Jameson, J. Am. Chem. Soc. 46:2475 (1924)
6. Lewis, G. N., Valence and the Structure of Atoms and Molecules, A. C. S. Monograph, The Chemical Catalog Co., New York, 1923
7. Carothers, J. Am. Chem. Soc. 46:2226 (1924)

sults, according to Lucas, as a result of the greater attraction of the methyl group for electrons than of the ethyl group, and the persistence of this greater attraction for electrons through the ethylene carbon to which it is attached.

C. The Theory of Partial Polarity of the Ethylene Bond.[8, 9, 1]

From a consideration of the heats of combustion of olefines, and the arrangement of forces around carbon atoms as revealed by the study of the relative electronegativities of organic radicals, Kharasch advanced the theory of partial polarity of the ethylene bond. This theory has been advanced in the form of seven postulates, viz:

Postulate I. There is a definite polarity at the double bond, so that the unsaturated derivatives of the ethylene type have a definite polarization in at least one part of the molecule.

This postulate is substantiated by the directive addition reactions of ethylene compounds.

Postulate II. In the case where the radicals attached to the carbon atoms of the double bond are about the same in electronegativity, it is possible to produce either of the following electromeric forms: and

An illuminating though brief discussion of this postulate is given by Kharasch and Darkis.[1] "These two forms are electroisomers. At no time do we assume, however, that these two forms are in equilibrium. This postulate implies that if by the addition of a molecule of HX to an ethylene derivative,

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8. Kharasch and Sher, J. Phys. Chem. 29:635 (1925)
9. Kharasch and Marker, J. Am. Chem. Soc. 48:3130 (1926)

$R:C :: C:R_1$, we obtain two products, $R:C : C:R_1$ (X, H) and $R:C : C:R_1$ (H, X), then they arise through the presence in the solution of two electro-isomers: $R:C : C:R_1$ and $R:C : C:R_1$, respectively. It is implied, also, that one of the electro-isomers is more stable and that, while it is possible to transform one electro-isomer into another, the two are not in equilibrium, for the transformation of one into the other would be accompanied by a change in the energy of the system."

Postulate III. The second pair of electrons constituting the double bond is always held in outer energy levels of one of the carbon atoms and some closer inner energy levels of the other, the particular level depending upon the nature of the radicals attached to the double bond.

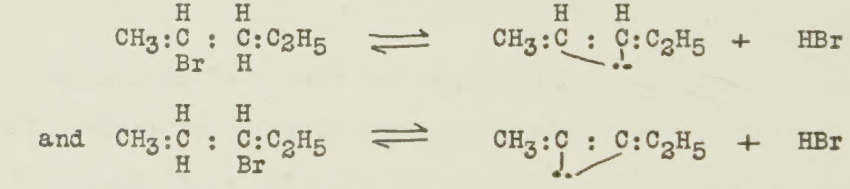
Postulate IV. The relative position of the second pair of valence electrons of the double bond depends upon the nature of radicals attached to it in such a way that they are always on the carbon atom opposite to that carrying the most electronegative radicals.

This postulate distinguishes the theory of partial polarity from any of those based upon the theories of Lewis. The postulate is supported by many facts, viz: The substitution of an electronegative radical as phenyl or bromine decreases the electronegativity of the methyl radical. It is also borne out by a study of addition reactions of ethylene derivatives.

Postulate V. Alkyl and aryl radicals are more electronegative than a hydrogen atom. Lewis considers hydrogen to be more negative than the methyl radical since methyl alcohol is a weaker acid than water. Valid objections have been advanced against

this method of assigning electronegativity values to organic radicals.[1] It has been pointed out that not only does it lead to erroneous conclusions regarding ethylene bond addition reactions, but it also leads to anomolies in placing certain radicals. For instance, hydrogen is more positive than a phenyl radical if one applies this method of determining electronegativity values to water and phenol. But if one considers instead formic and benzoic acid, quite the opposite conclusion will be drawn since K_a formic acid is 2.14×10^{-4}, whereas K_a benzoic acid is 6.6×10^{-5}.

Postulate VI. In the formation of an unsaturated derivative from an alkyl halide, it is assumed that the halogen is removed, taking with it the pair of valence electrons, and the hydrogen drops off to maintain the electrical neutrality of the molecule. By applying this postulate to the formation of 2-pentene, it can be seen that a different product is obtained from each of the bromopentanes:

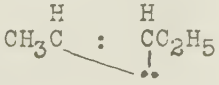


Whether both forms of olefines can exist depends upon the difference in electronegativity of the groups about one ethylene carbon and the electronegativity of the groups about the other. If the difference is small, it is possible to isolate both forms, one of which, however, is more stable. If the difference is large, only one form can exist.

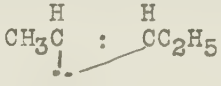
Postulate VII. In case the radicals attached to the carbon

atoms of the double bond are all different, the same principles apply as were developed for compounds in which two radicals of the same type were assumed to be attached to a carbon atom.

A consideration of Postulate IV elucidates the essential point of difference between the two theories considered. According to the theory of partial polarity, a strongly electronegative group has a tendency to draw the electrons away from the carbon to which it is attached. Not only are the two electrons which constitute the bond between this electronegative group and the carbon atom subject to this tendency, but the other valence electrons about the carbon atom also have a tendency to be displaced outward. Remembering that methyl has a stronger attraction for electrons than the ethyl radical, the following structure would be assigned to 2-pentene:



Lucas, postulating an attractive force which persists through the ethylene carbon, assigns the structure:



Since the only test of a theory is the accuracy with which it fits the facts, it is of interest to compare these two theories which differ so fundamentally, in the light of reactions of the ethylene bond compounds, the course of these reactions having already been determined. In the following table, a correct theory prediction is marked by a (+), an incorrect prediction by a (-).

Olefine	Added	Chief Product	Lewis-Lucas	Partial Pol.
$CH_2::CHI$	HI	$CH_3:CHI_2$	—	+
$C_6H_5:CH::CH_2$	HBr	$C_6H_5:CHBr:CH_3$	—	+
$CH_2::CClCH_3$	HI	$CH_3:CCl_2CH_3$	—	+
$CH_3:CBr::CH_2$	HBr	$CH_3:CBr_2:CH_3$	—	+
$CH_3:CCl::CH_2$	HBr	$CH_3:CClBr:CH_3$	—	+
$CH_3:CH::CH:C_2H_5$	HBr	$CH_3:CH_2CHBr:C_2H_5$	+	— *

Because the theory of partial polarity fits the facts so well, it was deemed advisable to check the work of Lucas and Moyse[1] in which they found results at variance with the predictions of the theory. A further investigation of this reaction by Kharasch and Darkis[2] demonstrated the existence of two forms of 2-pentene. The form used by Lucas and Moyse in their work on 2-pentene is capable, by the action of heat and light, of at least partial transformation into another form which reacts according to the predictions of the theory of partial polarity. We shall now consider the work which answered the objection raised by the reaction of 2-pentene with hydrogen bromide to the theory of partial polarity, and also established the existence of electro-isomeric forms of the compound.

Addition of Unsymmetrical Reagents to 2-Pentene.

A. The Theory of Partial Polarity and 2-Pentene.

A study of 2-pentene in the light of the postulates un-

* Instead of an exception to the theory of partial polarity, a further study of this compound has led to the discovery of the existence of electro-isomers.

derlying the theory of partial polarity reveals a dissymmetry in the groups attached to each carbon of the ethylene bond.

$$CH_3{:}\overset{H}{C} :: \overset{H}{C}{:}C_2H_5$$

Because the electronegativity of the methyl group differs but little from that of the ethyl group, it is to be expected that each carbon of the ethylene bond will be affected almost alike by the radicals attached to them. It follows from Postulate II of the theory of partial polarity that this compound can therefore exist in two electro-isomeric forms, viz:

$$CH_3\,\overset{H}{C} : \overset{H}{C}\,C_2H_5 \qquad \text{I}$$

and

$$CH_3\,\overset{H}{C} : \overset{H}{C}\,C_2H_5 \qquad \text{II}$$

In the future we shall refer to form I as 3-neg-2-pentene and to form II as 2-neg-2-pentene. If the theory of partial polarity is correct, Postulate VI indicates, further, the method by which these two forms may be obtained. If 3-bromopentane is treated with alchoholic potassium hydroxide, 2-neg-2-pentene should result, e. g.,

$$H_3C{:}\overset{H}{C} : \overset{H}{C}{:}C_2H_5 + KOH \longrightarrow H_3C{:}\overset{H}{C} : \overset{H}{C}{:}C_2H_5 + KBr + H_2O$$
$$\qquad\qquad\qquad\quad Br$$

In a similar way it should be possible to obtain 3-neg-2-pentene by a like reaction with 2-bromopentane.

In the light of this development of the theory of partial polarity, the work of Lucas is readily explicable.

B. Lucas & Moyse's[2] Work on 2-Pentene.

These investigators prepared 2-pentene from 3-bromopentane by the action of alchoholic potassium hydroxide. The 2-pentene so obtained reacted with hydrogen bromide in a solu-

tion of glacial acetic acid to yield a mixture of 78% of 3-bromopentane and 22% of 2-bromopentane. Later investigations have indicated that the reaction yields 3-bromopentane almost quantitatively when other solvents such as carbon tetrachloride and hexane are substituted for acetic acid.

Because the method used by Lucas and Moyse[2] yields 2-neg-2-pentene, the results obtained by the addition of hydrogen bromide are in perfect accord with the theory of partial polarity.

Lucas and his co-workers[10] have also prepared 2-pentene from 2-bromopentane. The 1-pentene which is also formed in this reaction was not separated. The amount of it was estimated by determining the refractive index (N_D^{20} 1.4431) of the mixture of monobrompentanes formed in the addition of hydrogen bromide. This work was carried out before the theory of partial polarity was advanced and the existence of electro-isomers of 2-pentene proven. The mixture obtained by them is very probably a mixture of 1-bromopentane (N_D^{20} 1.4444) and 2-bromopentane (N_D^{20} 1.4416) as would be predicted by the theory of partial polarity, instead of 2-bromopentane and 3-bromopentane (N_D^{20} 1.4443) which they assume.

C. Kharasch and Darkis' Work on 2-Pentene.[1, 11]

These investigators prepared 2-neg-2-pentene from 3-bromopentane by the same method employed by Lucas. They confirmed the results obtained by Lucas on the addition of hydro-

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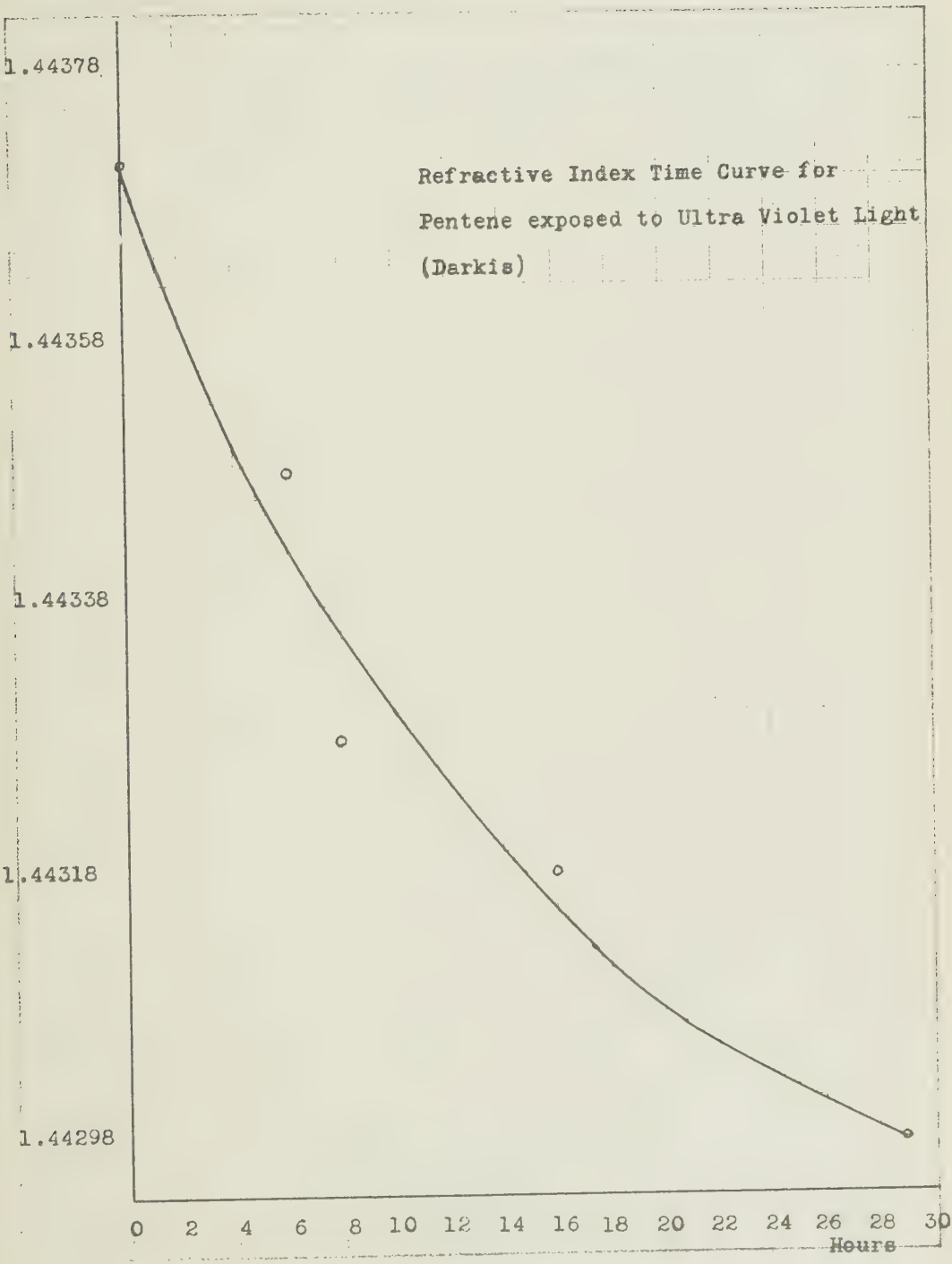
10. Lucas, Simpson, Carter, J. Am. Chem. Soc. 47:1463 (1925).
11. Kharasch and Darkis, Ph. D. Thesis, Univ. of Maryland, 1927.

GRAPH 1


Refractive Index
1.44378
1.44358
1.44338
1.44318
1.44298
Refractive Index Time Curve for
Pentene exposed to Ultra Violet Light
(Darkis)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Hours

gen bromide to this compound in glacial acetic acid solution. It was further determined that heat and light will to some extent convert 3-neg-2-pentene. This conversion is evinced by a greater proportion of 2-bromopentane in the reaction product obtained by the addition of hydrogen bromide. Graph I shows diagrammatically the action of heat and light in this conversion.

D. Carr and Co-workers on 3-pentene.[12]

By the action of alchoholic potassium hydroxide on 2-bromopentane and 3-bromopentane, Carr obtained both 3-neg-2-pentene* and 3-neg-2 pentene. Decided differences in the physical constants and reactions of the two electro-isomers were noted. It was also observed that extreme care was necessary in the selection of starting material for the preparation of these compounds. Variations in procedure were introduced, such as the formation of 2-pentene from the carbinol and 80% sulfuric acid. It became increasingly evident that the preparation of these electro-isomers cannot be accomplished by any method which is at all drastic; further, that if a mixture of structural isomers of any intermediate product is obtained in an attempt to prepare the two electro-isomeric forms of 3-pentene, with the exception of the unavoidable mixture of 1-pentene and 3-neg-2-pentene, such a mixture cannot be completely purified.

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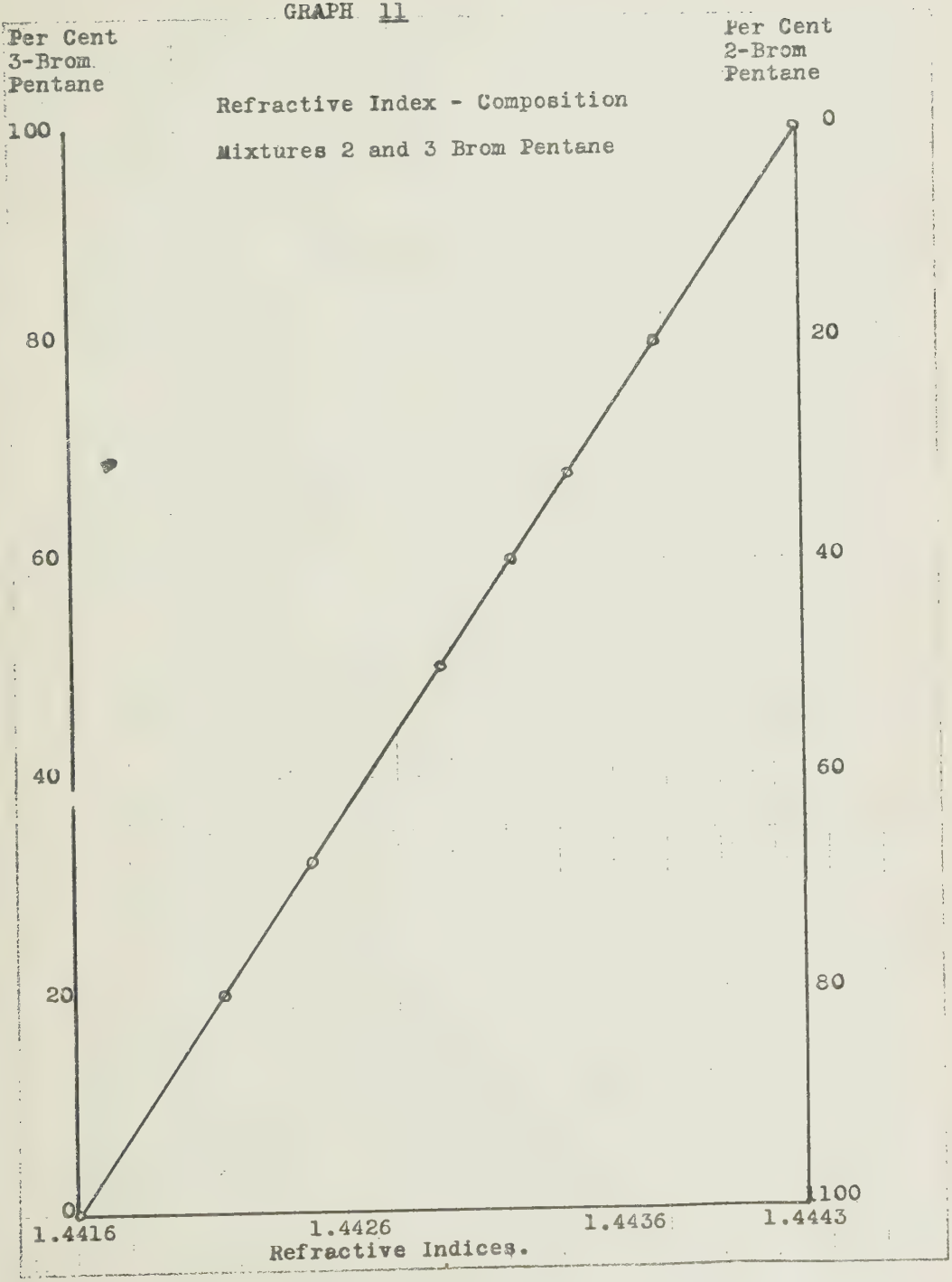
12. Carr, Abstract at Swampscott Meeting, Am. Chem. Soc., 1928 Private Communications to Dr. Kharasch.

* 1-Pentene present as an impurity was removed by repeated fractionations of an aziotropic mixture of the two pentenes in methyl alcohol.

GRAPH II


Per Cent
3-Brom
Pentane
Per Cent
2-Brom
Pentane
Refractive Index - Composition
Mixtures 2 and 3 Brom Pentane
100
80
60
40
20
0
0
20
40
60
80
100
1.4416
1.4426
1.4436
1.4443
Refractive Indices.

In the experimental work described in this paper, the purity of the product obtained in each step was determined by means of the refractometer and, when a mixture of structural isomers was indicated, the material was immediately discarded. No reliance can be placed on the boiling points and density determinations as an indication of purity in the preparation of these electromers because these physical constants are nearly identical for corresponding intermediates in the preparation of each electroisomer.

E. Further Evidence of the Existence of Electro-Isomers.

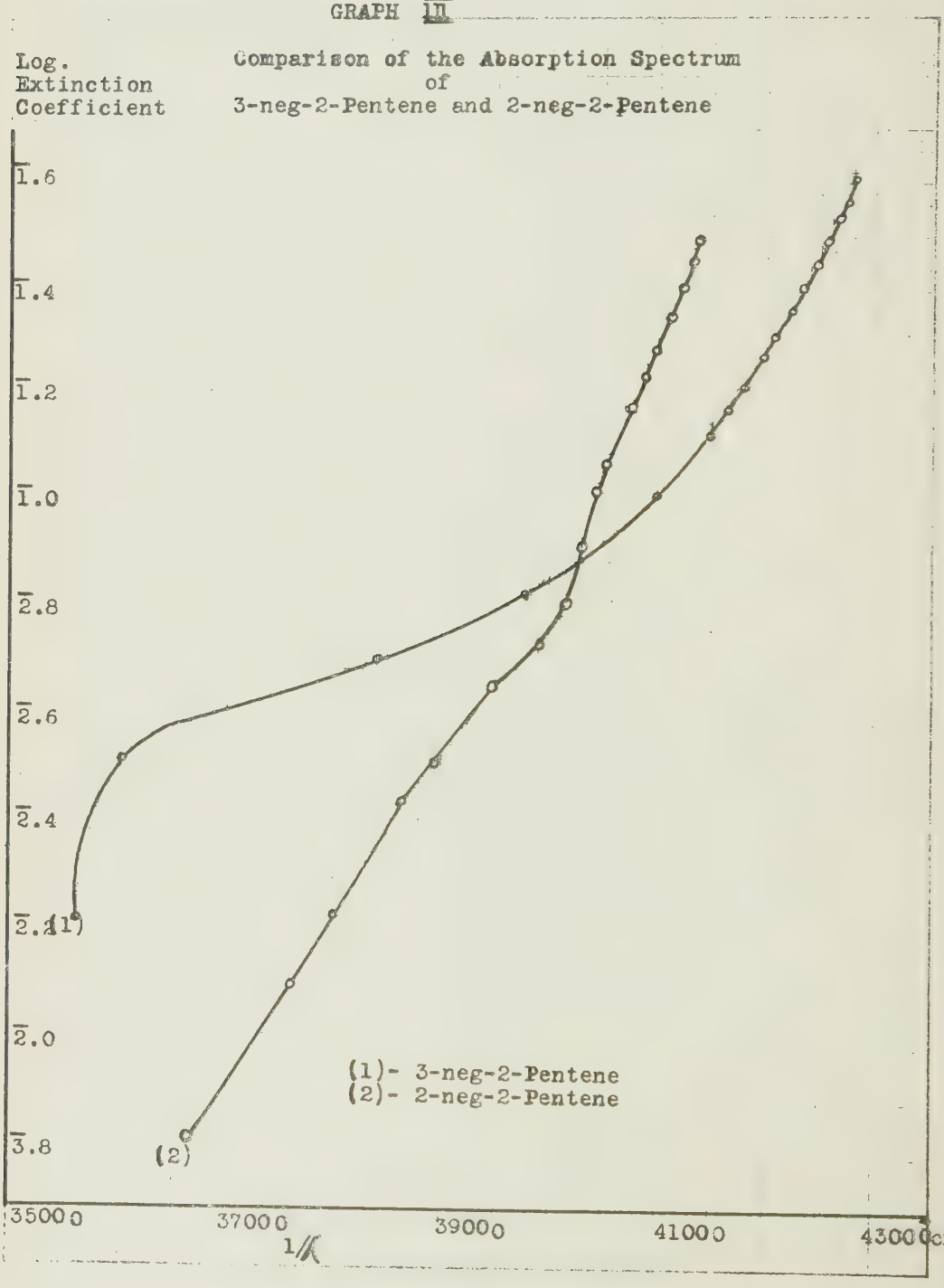
Because of the extreme importance attached to the problem of the isolation and the proof of the structure of the electroisomers of 2-pentene, it was deemed advisable to repeat the former work and extend the study of the reactions of these compounds to the addition of hydrogen chloride. Accordingly, the electromers were prepared by the same method employed by the previous investigators. Several attempts to prepare each electromer failed, however, because the necessary precautions were not observed closely enough. Quite some difficulty was also experienced in obtaining products of the high degree of purity required in these preparations.

The 2-pentene obtained by the action of alcoholic potassium hydroxide on 2-bromopentane was found to have a refractive index, N_D^{30}, of 1.3785, whereas 3-bromopentane yielded a pentene, the refractive index, N_D^{30}, of which was 1.3796. This difference confirms the data obtained by Carr and is greater than could be claimed as due to experimental error. Carr also

reports a difference of nearly 1° in the boiling points of the azeotropic mixtures of each electromer in methyl alcohol. To further convince ourselves that two distinct forms of 2-pentene exist, absorption spectra studies were made. Hexane which showed no absorption of light of the wave length transmitted (6000 Å - 2100 Å) was used as a solvent. Solutions of the 2-pentenes in hexane varying in the concentration of the former between 15% and 35% were compared with water. The two electromers show a decided difference in their absorption spectra as evinced by Graph III. This graph was constructed by plotting the logarithm of the extinction coefficient against the reciprocal of the wave length. While the graph from the data obtained by us does not coincide exactly with that obtained by Carr (IV), a qualitative confirmation of her work can justifiably be claimed. It might be added in justice to the results obtained by Carr that my work was more cursory and was carried out under adverse weather conditions. A high dew point and a room temperature very close to the boiling point of the two pentenes made the attainment of accurate concentrations of pentene solutions extremely difficult.

Because of the differences in the physical constants of the pentenes prepared from 3-bromopentane and 2-bromopentane, there can be no doubt that they are not identical compounds. The addition of unsymmetrical reagents confirms such a conclusion. Before discussing their reactions with hydrogen halides, however, let us consider the possibility of impurities which could easily give rise to the differences observed. In the preparation of 3-neg-2-pentene from 2-bromopentane, some 1-pen-

GRAPH III


Log. Extinction Coefficient
Comparison of the Absorption Spectrum of 3-neg-2-Pentene and 2-neg-2-Pentene
1.6
1.4
1.2
1.0
2.8
2.6
2.4
2.2
2.0
3.8
(1)
(2)
(1)- 3-neg-2-Pentene
(2)- 2-neg-2-Pentene
35000
37000
39000
41000
43000 cm⁻¹
1/λ

tene is also formed. The completeness of the separation of the two structural isomers, 1-pentene and 2-pentene, can naturally be questioned. Fortunately, this question of the purity of the two 2-pentenes is easily and conclusively answered by the fact that both 3-neg-2-pentene and 2-neg-2-pentene yield 2-3-dibromopentane by the addition of bromine, whereas 1-pentene yields 1-2-dibromopentane. Since the two dibromopentanes have different physical constants, residual 1-pentene is thus detectable. A portion of each of the two 2-pentenes, the physical constants of which indicated them to be different compounds, were converted into the dibromo derivatives. The physical constants obtained from these derivatives are tabulated below:

TABLE I

Showing Absence of Structural Isomers as Impurity

	Dibromo-Derivatives Formed From		Literature*	
	3-neg-2-pentene	2-neg-2-pentene	1-2-dibromo-pentane	2-3-dibromo-pentane
B. P.	179.5-181° (corr.)	178.5-180° (corr.)	184° [13]	175° [16] 178-179° [17] 180.2-180.8° [18]
N_D^{20}	1.5069	1.5069	1.5088(21°) [13]	1.5074 [17] 1.5093(17°) [18] 1.5098 [18]
D_4^{20}	1.647	1.646	$D_4^{17.2}$ 1.6766 [14] D_4^{20} 1.6782 [15]	N^{15} 1.738 [19]
N_F-N_C	0.0118	0.0118		

See next page for references.

* The wide range of values for the boiling points and refrac-

An inspection of the above table will show the justification for claiming that the two 2-pentenes, the physical constants of which are different, give the same dibromo derivatives. The natural inference which follows is that 2-pentene does exist in two different forms.

The theory of partial polarity assigns to these forms the structures:

The correctness of this assignment of structure can be tested by the addition of unsymmetrical reagents. Two different products should result. The addition of hydrogen bromide confirmed the work of previous investigators and it was further extended by a study of hydrogen chloride additions to each form. To obtain the physical constants of 2-chloro and 3 chloropentane an attempt was made to prepare them from the corresponding carbinols by the action of hydrogen chloride in a manner identical with that used to obtain the bromo-derivatives. This method how-

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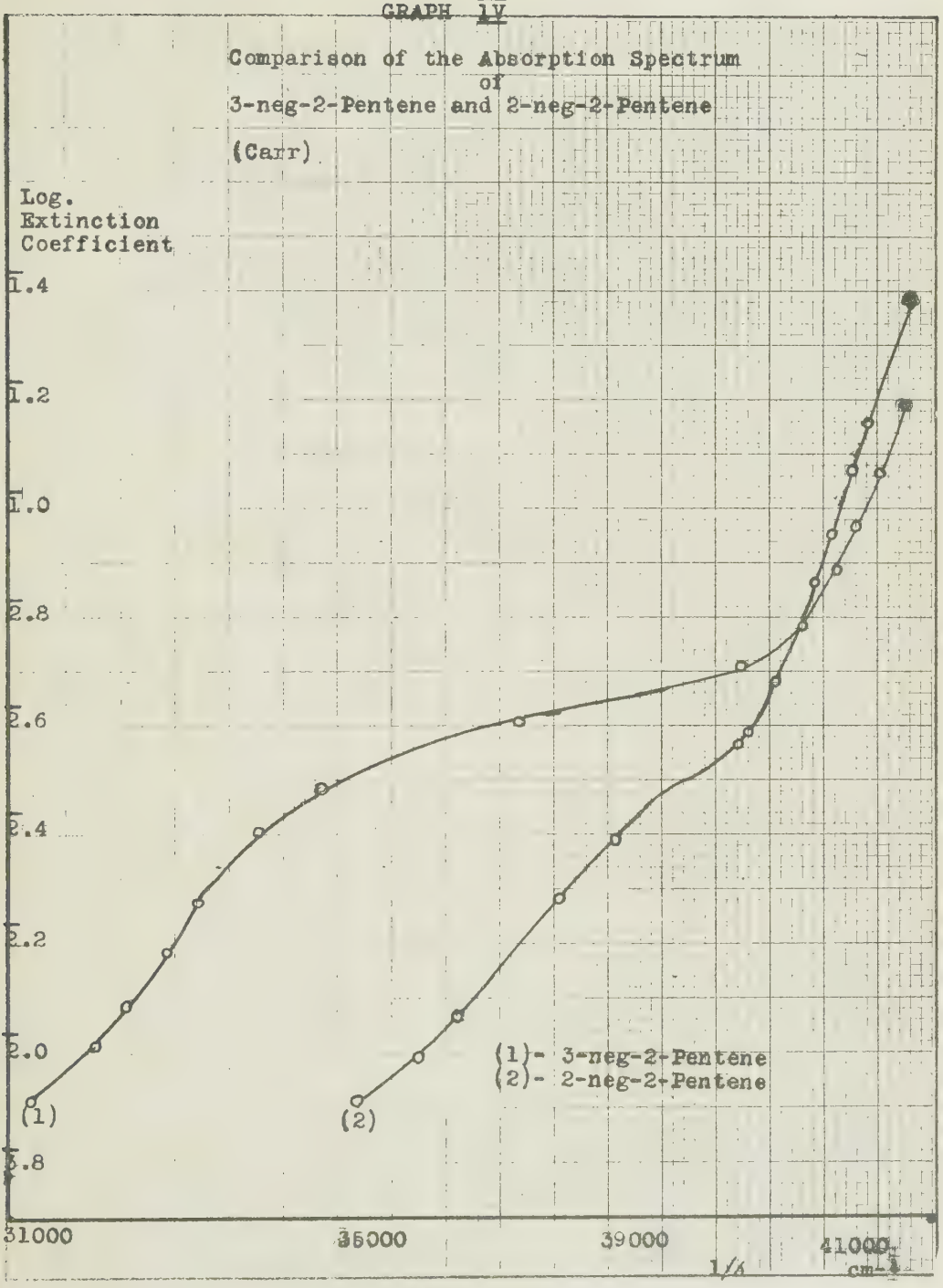
tive index of 2-3-dibromopentane reported in the literature is very probably due to varying amounts of 1-2-dibromopentane present as an impurity. The more drastic methods used by some of these investigators[18] were found to be highly satisfactory in the attainment of 2-pentene free from the contamination of structural isomers. Indeed, the work of Norris and Reuter has been repeated by Carr and the physical constants of the dibromo-derivative described by them were obtained, but the pentene from which it was prepared had a refractive index, N_D^{20}, of 1.3794, which gave evidence of some impurity present.

See page 14.

13. Kirrman, Bull. Soc. Chim. (4) 39:989 (1926)
14. Van Risseghem, C. R. 158:1696
15. Rosanow, [illegible] 48:182 C. 1923 I, 1490
16. International Critical Tables I
17. Wagner and Saytzeff, Ann. 179:307 (1875)
18. Norris and Reuter, J. Am. Chem. Soc. 49:2630 (1927)
19. Brochet, Bl. (3) 7:567

GRAPH IV


Comparison of the Absorption Spectrum
of
3-neg-2-Pentene and 2-neg-2-Pentene
(Carr)
Log.
Extinction
Coefficient
1.4
1.2
1.0
2.8
2.6
2.4
2.2
2.0
1.8
(1)
(2)
(1)- 3-neg-2-Pentene
(2)- 2-neg-2-Pentene
31000
35000
39000
41000
1/λ
cm-1

ever did not result in sufficiently high yields to be practical. They were then prepared by the action of anhydrous zinc chloride and concentrated hydrochloric acid at room temperature on the corresponding carbinols. Hydrogen chloride was then added to 2-neg-2-pentene and to 3-neg-2-pentene using glacial acetic acid as a solvent in both cases.

A comparison of the physical constants of the addition products of hydrogen chloride to the two forms of 2-pentene is made in the following table:*

TABLE II

Physical Constants

of 2-Chloropentane and 3-Chloropentane

	B. P.	N_D^{20}
3-chloropentane and $ZnCl_2$ HCl aq.	97.2°/750 mm.	1.4103
2-chloropentane and $ZnCl_2$ HCl aq.	95.2°/750 mm.	1.4074
2-neg-2-pentene and HCl	97.3°/745 mm.	1.4098
3-neg-2-pentene and HCl	95°/747 mm.	1.4075

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* The boiling point of 2-chloropentane and 3-chloropentane listed in the International Critical Tables is 105°. This value was obtained by Wagner and Saizew (Ann. 179:321) by heating the corresponding carbinols with phosphorus pentachloride. They state that very small quantities of material were used for this work. The drastic method of preparation and the quantities employed give rise to the suspicion that they were dealing with isomeric compounds. Furthermore, their observation of the boiling points might be in error in view of the small amount of material they had at their disposal. This suspicion is substantiated by the work of Przewalski (J. Russ. Phys. Chem. Geo. 40:1105; C II, 794, 1909) who obtained 2-chloropentane by the method used by Wagner and Saizew. The boiling point reported by this investigator is 96°-97° under 747 mm., and the refrac-

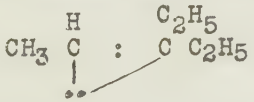
D. Are the electromers cis-trans isomers?

That some chemists would attribute the different action of the two forms of 3-pentene as due to cis-trans isomerism is recognized. This possibility has been discussed by Kharasch and Darkis[1] whom I quote:

"It is readily noticed that 3-pentene may exist in two forms, cis and trans. It may, therefore, be argued that the two electromers are cis-trans isomers. The data at hand do not allow one to draw such far reaching conclusion. For that would imply that cis-trans isomers would add an unsymmetrical reagent in a different manner. The fact that bromine addition products are the same would argue against such a conclusion. However, bromine is a poor reagent for such a purpose, and the oxidation of these electromers with permanganate, a reagent which is less likely to cause shifts from cis to trans, is now being studied."

For the reasons above cited a study of the addition reactions of hydrogen chloride to 3-ethyl-2-pentene was made because this compound does not exist in two stereoisomeric forms. Postulate II of the theory of partial polarity of the ethylene bond requires, however, that the radicals attached to the carbon atoms of the double bond must be of about the same order of electronegativity if the compound is to exist in two electroisomeric forms.

The results obtained in the addition of hydrogen chloride to 3-ethyl-2-pentene confirm the work of Lucas[20] and indicate that this compound exists only in the following form:



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tive index, $N_D^{19.5}$, 1.4062. In view of the possibility of the formation of isomeric substances, no great reliance can be placed upon the value of this refractive index.

20. Lucas, J., J. Am. Chem. Soc. 51:248 (1929)

No change in the directive influence exerted by this compound toward unsymmetrical reagents was observed by the action of heat and light. In the data obtained by us in the study of this reaction, it was observed that only on exposure to ultra-violet light did the 3-ethyl-2-pentene yield a product which differed in physical constants from that indicating quantitative formation of 3-chloro-3-ethyl pentane. A higher index of refraction for the hydrogen chloride addition product was obtained by such treatment. Since 2-chloro-3-ethyl pentane has a lower refraction index than 3-chloro-3-ethyl pentane, a mixture of these two compounds is not indicated. It is quite possible that polymerization of 3-ethyl-2-pentene takes place by the action of ultra-violet light.

Because 3-ethyl-2-pentene adds hydrogen chloride to form 3-chloro-3-ethyl pentane, an interesting corollary follows from the theory of partial polarity, viz: the groups involved in determining the electronic structure of 3-ethyl-2-pentene are in the following order of electronegativity:

CH_3 ——:
C_2H_5 ———:
H ————:

Since the determined structure of 3-ethyl-2-pentene is

the following relationship exists in the electronegativities of the involved groups, viz: $(CH_3) + (H) < 2\ (C_2H_5)$. This indicates that the ethyl group is decidedly more electronegative than a hydrogen atom.

EXPERIMENTAL

A. Preparation of 2-Pentanol.

Commercial 2-pentanol was found to be unsatisfactory for the preparation of 3-neg-2-pentene even after purification by means of fractional distillation. This material was therefore prepared by the method of Woods and Scarf.[21] 2-Pentanol was obtained by means of a Grignard reaction between n-propyl bromide, b. p. 71°-71.4°, acetaldehyde, b.p. 20.5°-21.0°, and magnesium (Kahlbaum).

$$C_3H_7MgBr + CH_3CHO \longrightarrow C_3H_7CH(OMgBr)CH_3$$

$$C_3H_7CH(OMgBr)CH_3 + H_2O \longrightarrow C_3H_7CH(OH)CH_3 + MgOHBr$$

The carbinol was purified by two distillations. It boiled at 118°-118.5° under 750 mm. The refractive index, N_D^{20}, was 1.4061.

B. Preparation of 2-Bromopentane.

Pentanol-2 was converted into the corresponding bromide by saturating it with dry hydrogen bromide. The saturation was carried out at 10°. The reaction mixture was then placed in a water bath at 60°. Constant pressure inside the flask was maintained by attaching a rubber balloon to the exit tube of the saturation flask. An increased pressure causes the formation of a mixture of monobromopentanes. Several saturations are necessary. A lower layer of 2-bromopentane separates in the course of the reaction and the amount of this lower layer indicates the progress of the reaction.

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21. Woods and Scarf, J. Soc. Chem. Ind., 42:13T (1923)
Lucas, Simpson and Carter, J. Am. Chem.Soc. 47:1462 (1925)

$$H_3C{:}CH{:}(OH){:}C_3H_7 + HBr \longrightarrow H_3C{:}CHBr{:}C_3H_7 + H_2O$$

The reaction mixture was then cooled and washed with water at 0°. Unreacted carbinol was removed by washing with concentrated sulfuric acid at -10°. The 2-bromopentane was washed with water, with dilute aqueous sodium carbonate, followed by three more washings with water. The material was then dried at 0°, by means of anhydrous sodium sulfate and filtered through sodium sulfate into a distilling flask. It was distilled under reduced pressure to avoid decomposition and the distillate was then distilled at atmospheric pressure. The boiling point of the 2-bromopentane used in the preparation of 3-neg-2-pentene was 116.5°-117.5° at 745 mm. The refractive index, N_D^{20}, was 1.4409.

C. Preparation of 3-Neg-2-Pentene.[8]

The action of alcoholic potassium hydroxide on 2-bromopentane forms a mixture of 1-pentene and 3-neg-2-pentene. This mixture was obtained by dropping 2-bromopentane (302g.) slowly into a solution of potassium hydroxide (336 g.) in 600 cc. of absolute methyl alcohol. The reaction flask was fitted with a long reflux condenser to the exit of which was attached a downward condenser. The reaction mixture was heated at 110°-115° on an oil bath.

$$CH_3{:}CHBr{:}C_3H_7 + KOH \longrightarrow CH_3{:}\overset{H}{C} :: \overset{H}{C}{:}C_3H_5 + KBr + H_2O$$

and

$$CH_3{:}CHBr{:}C_3H_7 + KOH \longrightarrow \overset{H}{HC} :: \overset{H}{C}{:}C_3H_7 + KBr + H_2O$$

Vapors from the mixture were fractionated by keeping the reflux condenser at 40°. The distillate was collected in absolute

methyl alcohol. The separation of the structural isomers obtained presented one of the chief difficulties in the preparation of 3-neg-2-pentene. With the aid of Mr. G. Reppert quite a number of fractionating columns were made and tried. A four bulb Le Bel Hinneger column was finally chosen. After six fractional distillations of an azeotropic mixture of the pentenes in methyl alcohol, a fraction was obtained, b. p. 30.3°-30.8° (corr.) which had a refractive index, N_D^{20}, of 1.3785. This refractive index checks the value obtained by Carr.[10] The boiling point, however, was 0.4° lower than that observed by her.

D. Reactions of 3-Neg-2-Pentene.

1. Bromine and 3-neg-2-pentene.

3-Neg-2-pentene (10 g.) was dissolved in 25 g. of glacial acetic acid. Bromine dissolved in glacial acetic acid was added drop by drop to this solution. The temperature was kept at 15°. Almost instantaneous decolorization of the added solution gave evidence of the speed of the addition reaction. Addition of the bromine solution was continued until the reaction mixture acquired a permanent faint yellowish color. Water (200 g.) was then added and the separated lower layer of dibromopentane was purified by washing once with water, once with a very dilute solution of sodium thiosulfate and thrice with water. The dibromopentane was then dried with anhydrous sodium sulfate and distilled in vacuo. The physical constants determined were: refraction index, N_D^{20}, 1.5068; d_4^{20}, 1.647; mean dispersion, N_F-N_C, 0.0118; and boiling point 178.5°-181°

(corr.) at 760 mm.

2. Hydrogen Chloride and 3-Neg-2-Pentene.

An attempt to add hydrogen chloride to 3-neg-2-pentene without a solvent was unsuccessful because of the slow reaction rate. Glacial acetic acid was therefore used to accelerate the reaction.

3-neg-2-pentene (8 g.), dried by means of anhydrous sodium sulfate at 0°, was added to 59 g. of a 15.4% solution of hydrogen chloride in glacial acetic acid. The reaction mixture was kept at -10° for two hours. The temperature was then raised to 5°. After twenty hours the reaction product was separated and purified by washing once with water, three times with concentrated sulfuric acid at -10°, once with water, once with dilute aqueous sodium carbonate, and thrice with water. The material was then dried by means of anhydrous sodium sulfate, and distilled under vacuo. The physical constants then determined were: boiling point, 94.5°-95° at 747 mm. and refractive index, N_D^{20}, 1.4075.

E. Preparation of 3-Bromopentane.[1, 2]

Diethyl carbinol used as the starting material was a special preparation obtained from the Eastman Kodak Co. It had been prepared from ethyl bromide and propionaldehyde by means of a Grignard reaction. The refractive index, N_D^{20}, of the carbinol was 1.4093. 3-Bromopentane was prepared from the carbinol in the identical manner by which 2-bromopentane was obtained

from 2-pentanol.* The boiling point of the purified 3-bromopentane was 117°-118° at 745 mm. and the refractive index, N_D^{20}, was 1.4443. The refractive index of this material checks exactly the value obtained by previous investigators.

F. Preparation of 2-Neg-2-Pentene. [1, 2]

The unsaturated 2-neg-2-pentene was obtained by the same method used in preparing 3-neg-2-pentene from 2-bromopentane.(*) Pure 2-neg-2-pentene results, however, instead of a mixture of 1-pentene and 2-pentene.

$$C_2H_5{:}CHBr{:}C_2H_5 + KOH\ (alc.) \longrightarrow H_3C{:}\overset{H}{C} :: \overset{H}{C}{:}C_2H_5 + KBr + H_2O$$

The refractive index, N_D^{20}, of the 2-neg-2-pentene obtained was 1.3796.

G. Reactions of 2-Neg-2-Pentene.

1. Bromine and 2-Neg-2-Pentene.

2-Neg-2-pentene (10 g.) was dissolved in 25 g. of glacial acetic acid. A solution of bromine in glacial acetic acid was added drop by drop. The reaction mixture was kept at 15°. On completion of the addition reaction, the dibromopentane was subjected to the same purification processes as those previously described for the dibromo-derivatives of 3-neg-2-pentene. The physical constants of the purified product were: refractive index, N_D^{20}, 1.5069; d_4^{20}, 1.646; mean dispersion 0.0118; and boiling point, 178.5°-180° (corr.).

2. Hydrogen Chloride and 2-Neg-2-Pentene.

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* Refer to B, experimental part, this paper.
(*) Refer to C, experimental part, this paper.

2-Neg-2-pentene (10 g.) was added to 70g. of a 15.4% solution of hydrogen chloride in glacial acetic acid. The reaction mixture was kept at -10° for two hours. The temperature was then raised to 5°. After twenty hours, the reaction product was separated and purified by washing once with water, three times with concentrated sulfuric acid at -10°, once with water, once with dilute aqueous sodium carbonate, and thrice with water. The material was then dried by means of anhydrous sodium sulfate and distilled under vacuo. The material had a refractive index, N_D^{20}, of 1.4098, and a boiling point of 97.3° under 747 mm.

H. Preparation of 2-Chloropentane.

2-Pentanol (15 g.) was placed in a 200 cc. round bottom flask fitted with a stirrer. Three equal portions of concentrated hydrochloric acid (40 g.) and anhydrous zinc chloride (13 g.) were added at room temperature over a period of ten hours. After thirty-two hours, during which the reaction mixture was continuously stirred, the upper layer was separated, washed once with water, three times with concentrated sulfuric acid at -10°, once with water, once with dilute aqueous sodium carbonate, and thrice with water. The material was dried by means of anhydrous sodium sulfate and distilled under vacuo. The yield of 2-chloropentane was almost quantitative. The 2-chloropentane boiled at 95.2° (corr.) at 750 mm. and had a refractive index, N_D^{20}, of 1.4075. A repetition of the preparation yielded a product which boiled at 94.5°-95.2° (corr.) at 753 mm. and had a refractive index, N_D^{20}, of 1.4073.

I. Preparation of 3-Chloropentane.

Simultaneously with the preparation of 2-chloropentane described in (H), 3-pentanol (15 g.) was treated in exactly the same manner. The preparation yielded 3-chloropentane which boiled at 96.8°-97° (corr.) at 753 mm. and had a refraction index, N_D^{20}, of 1.4100. A repetition of the preparation yielded a product which boiled at 96°-97.2° (corr.) at 750 mm. and possessed a refractive index, N_D^{20}, of 1.4103.

J. Preparation of 3-Ethyl-3-Pentanol.[22]

From 258 g. (3 moles) of diethyl ketone, b.p. 101°-103°, 330 g. (3 moles) of ethyl bromide, b.p. 38.4° at 745 mm., and 74 g. (3 moles) of magnesium (Kahlbaum) in 600 cc. of dry ether, there was obtained, following hydrolysis, 235 g. of crude 3-ethyl-3-pentanol distilling at 67.5°-72.5° at 50 mm. The crude material was washed three times with water at 0° to remove unreacted diethyl ketone. It was then dried by means of anhydrous sodium sulfate. The dried material was fractionated three times under reduced pressure. The boiling point of the final product was 73.0°-73.0° (corr.) at 50 mm. The refractive index of the material, N_D^{20}, was 1.43059.

K. Preparation of 3-Chloro-3-Ethyl Pentane.[17]

This product was obtained by stirring 12 g. (0.1 mole) of 3-ethyl-3-pentanol with concentrated hydrochloric acid and

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22. Brooks and Humphreys, J. Am. Chem. Soc. 40:835 (1918)
Schreiner, J. prakt. Chem. (2), 82:292 (1910)
Mazurewitsch, J. Russ. Phys. Chem. Soc. 42:1582(1910) C.I.,
Davies and Kipping, J. Chem. Soc. 99:298 (1911). 1500(1911)
Lucas, J., Am. Chem. Soc. 51:252 (1929)

anhydrous zinc chlorice. The hydrochloric acid and zinc chloride were added in five successive portions consisting of 20 g. of the former and 5 g. of the latter. The reaction was carried out at room temperature. After eighteen hours of continuous stirring, the upper layer of 3-chloro-3-ethyl pentane was separated. Hydrogen chloride was removed by washing five times with water. The material was dried by means of anhydrous sodium sulfate. It boiled at 81°-81.7° at 100 mm. The refractive index, N_D^{20}, was 1.43357.

L. 3-Ethyl-2-Pentene.[17]

To 232 g. (2 moles) of triethyl carbinol in a flask fitted with a reflux condenser, 245 g. (2.7 moles) of anhydrous oxalic acid was added. The mixture was heated on a water bath for five hours. The reaction proceeded smoothly. 3-ethyl-2-pentene was distilled from the reaction mixture. Water which distilled with the 3-ethyl-2-pentene was partially removed by cooling the distillate to -10° and decanting the pentene. The decanted material was filtered through a column of anhydrous sodium sulfate into a distilling flask containing five grams of sodium. The 3-ethyl-2-pentene distilled at 94.9°-95.3° (corr.) at 750 mm. The yield of purified product was 156 g. or 80% of the theoretical amount.

M. Reactions of 3-Ethyl-2-Pentene.[17]

Eight grams of dry hydrogen chloride were dissolved in thirty-nine grams of glacial acetic acid. This solution and eleven grams of 3-ethyl-2-pentene were placed in a glass stoppered bottle. The reaction mixture was kept at 5° for twelve

hours. The resulting heptyl chloride was purified by washing once with water to remove acetic acid and hydrogen chloride, three times with concentrated sulfuric acid at -10° to remove unreacted 3-ethyl-2-pentene. The sulfuric acid was removed by washing once with water, once with dilute aqueous sodium carbonate, followed by three washings with water. The heptyl chloride was dried with anhydrous potassium carbonate. The weight of the dried material was 14.6 g. (97.1%), and the refractive index, N_D^{20}, was 1.43334, corresponding to the 3-chloro-3-ethylpentane obtained from the carbinol.

Experiments identical with the one described above except in the treatment of the 3-ethyl-2-pentene before the addition of hydrogen chloride were performed.

3-Ethyl-2-pentene (12 g.) when heated in boiling water for five hours in a sealed tube yielded by the addition of hydrogen chloride in glacial acetic acid a heptyl chloride, the refractive index, N_D^{20}, of which was 1.43352. The yield was 92% of the theoretical amount.

3-Ethyl-2-pentene (11 g.) was dissolved in a parrafin oil, b. p. 160° at 36 mm. The solution was heated in a sealed tube at 145° for five hours. 3-ethyl-2-pentene was removed from the oil by two fractional distillations. It was then treated with hydrogen chloride in glacial acetic acid at 5°. The refractive index, N_D^{20}, of the product obtained was 1.43351, and the yield was 92% of the theoretical amount.

Eight grams of 3-ethyl-2-pentene were exposed to ultraviolet light for twenty-four hours. The temperature of the material was kept at 0° during the exposure. The addition of

hydrogen chloride in glacial acetic acid yielded a product, the refractive index, N_D^{20}, of which was 1.43403.

3-ethyl-2-pentene (8 g.) exposed to ultra-violet light at room temperature for the same period of time yielded 91% of the theoretically possible heptyl chloride, with a refractive index, N_D^{20}, of 1.43383.

Dry hydrogen chloride was passed directly into 10.5 g. of 3-ethyl-2-pentene. The reaction was carried out at room temperature and over a period of thirty hours. The reaction product purified in the manner described above had a refractive index, N_D^{20}, of 1.43357. The yield was 92% of that theoretically possible.

N. Absorption Spectra Studies.

A Hilger absorption spectrograph was used. Solutions of the two 2-pentenes in hexane were compared with water. The hexane used as a solvent exhibited no absorption of light in the range of wave lengths transmitted (6000 Å - 2100 Å). Solutions of the two 2-pentenes of the following concentrations were studied: (3-neg-2-pentene) 16.88%, 34.48% and 51.05%; (2-neg-2-pentene) 20.32% and 34.48%. It was found that highly concentrated solutions (more than 35%) were unsuitable because of the volatilization of the 2-pentene. A rotating sector was used to permit variation in the time of exposure. In constructing the graph from the data obtained, the logarithm of the extinction coefficient was plotted against the reciprocal of the wave length.

SUMMARY

1. Previous work on the addition of unsymmetrical reagents to 2-pentene is reviewed.

2. The apparent existence of two forms of 2-pentene, evinced by the previous study of these reactions is explained on the basis of the theory of partial polarity of the ethylene bond. These forms are called 3-neg-2-pentene and 2-neg-2-pentene. Their existence removes the factual evidence tending to invalidate the theory of partial polarity.

3. The existence of these two forms of 2-pentene is confirmed by the experimental work described. That they are different is shown by their differing physical constants and directive influences in the addition of unsymmetrical reagents. That these differences are not caused by the presence of structural isomers or other impurities is shown by the fact that the dibromo-derivatives of each are identical.

4. The addition of hydrogen chloride to 3-ethyl-2-pentene is described. The work of Lucas is confirmed. Addition reactions of this compound were studied because it does not exist in two stereoisomeric forms. The data obtained indicate that neither does it exist in two electro-isomeric forms. The data are in perfect accord with the theory of partial polarity, and are explained on the basis of this theory.

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